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Thesis

INVESTIGATIONS IN PYRROL CHEMISTRY

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I. INTRODUCTION.

The objects of my research are, primarily a study of potassium pyrrol from an analytical stand point, and secondarily, investigations as to why pure pyrrol is not obtained upon the hydrolysis of potassium pyrrol.

Pyrrol has been analyzed by Anderson (1). He found the boiling point of pyrrol to be 133 degrees centigrade and its density to be 1.077. He states that pyrrol reacts with platinum tetrachloride forming a dark precipitate but does not give any figures on the analysis of the dark precipitate. He also found that an alcoholic solution of pyrrol gives a white precipitate with mercuric chloride and also with cadmium chloride.

Anderson gives the following figures for the combustion of pyrrol in terms of percentage carbon and hydrogen:

	I	II	III	IV
C -	71.64%	71.42%	71.84%	71.61%
H -	8.17%	7.71%	7.77%	8.05%
	V	VI	VII	VIII
C -	71.54%	71.51%	71.54%	71.53%
H -	7.80%	7.74%	7.77%	7.78%

(1) Anderson, Annalen der Pharmacie; 105:354(1858)

The above percentages correspond to the formula C_8H_5N from which is obtained

C - 71.64%

H - 7.46%

N - 20.90%

Anderson evidently used 6 as the atomic weight of carbon. Carbon with an atomic weight of 12 did not come into use until 1860 - 1861 and Anderson did his work in 1858. Therefore, considering the atomic weight of carbon to be 12 instead of 6 we obtain the formula assigned to pyrrol by Baeyer in 1870, namely C_4H_5N .

For what Anderson termed impure or "bad smelling" pyrrol, he obtained a vapor density of 2.52 - 2.49; and for "good smelling" pyrrol a vapor density of 2.4 .

The following is an analysis of the precipitate formed when alcoholic pyrrol reacts with mercuric chloride as given by Anderson:

	Experimental	Calculated	
C -	7.89 - 7.57%	C_8 -	7.88%
H -	---- .81%	H_3 -	.82%

N	-	----	----	N	- 2.31%
Cl	-	----	----	Cl_4	- 23.31%
Hg	-	----	66.89%	Hg_4	- 65.68%

The precipitate for the above analysis was vacuum dried.

The following is an analysis of the precipitate formed when alcoholic pyrrol reacts with cadmium chloride:

$$2\ C_8H_5N + 3\ CdCl_2$$

	Experimental	Calculated
C -	23.25%	23.50%
H -	2.16%	2.44%

For further history of the work done on pyrrol, the reader is referred to Albert J. Plummer's Thesis on "Purification and Properties of Pyrrol". He covers the field of history thoroughly and I do not think it necessary for me to repeat what he has given.

From the evidence Dr. Holmes and I have collected, potassium pyrrol has been assumed to be a pure compound, but the product (pyrrol) formed on hydrolysis has not been found to be more than 95 percent pure. An analysis of potassium pyrrol is not to be found in the literature**. Dr. Holmes was able to obtain the above percent purity but not a higher percent of purity. This seems to indicate that the potassium pyrrol prepared in the laboratory is not a pure compound.

Potassium pyrrol has been discussed in detail under the work of Ciamician and Dennstedt on bone oil.(2). Potassium pyrrol is a beautiful yellowish crystalline solid, insoluble in ether and alcohol, and having an odor similar to that of pyrrol. The accepted formula for pyrrol is C_4H_4NH and that of potassium pyrrol is C_4H_4NK.

(2) Ciamician and Dennstedt; Ber.; 19:173 (1880)

** Meyer,V and Jacobson, P:"Lehrbuch der Organischen Chemie". Walter De Gruyter & Co. Berlin und Leipzig 1923. page 158.

Potassium pyrrol is formed from pyrrol by the addition of pure potassium. The following equation represents the reaction involved:

$$C_4H_4NH + K \longrightarrow C_4H_4NK + \tfrac{1}{2}H_2$$

An attempt has been made to find a solvent for potassium pyrrol so that it might be recrystallize and thus forming pure crystals but unfortunately no solvent was found.

II. PREPARATION OF POTASSIUM PYRROL

The pyrrol that was used in the preparation of the potassium pyrrol was prepared by the well known method of heating ammonium mucate with glycerine. On standing a year the pyrrol had turned dark colored and therefore was distilled in an atmosphere of hydrogen and a clear solution of pyrrol boiling at 129 degrees centigrade (Uncorrected) was obtained.

The distilled pyrrol was placed in a round-bottom 250 cc. flask which was attached to a reflux condenser. Fifty grams of the distilled pyrrol was used. Hydrogen gas was passed into the flask so there would be an atmosphere of hydrogen. The pyrrol was heated to boiling and then metallic potassium was added by dropping small pieces of the metal down through the reflux condenser tube. The flame was removed before the potassium was added. Care must be taken that the flask does not crack because the reaction is rather violent and fast. About twenty percent of the theoretical amount of potassium necessary to react with the pyrrol was added. When this amount of potassium is added a yellowish solid begins to form in the flask. At this point the flask was allowed to cool.

The cooled solid was washed once with absolute ether while stirring vigorously. The first ether wash was decanted off and the solid was placed in another flask containing ether and allowed to stay three days. The contents of the flask were stirred twice or more daily. At the end of this period the ether was decanted off, the solid was washed three more times with clean absolute ether, and placed in a dessicator containing barium perchlorate as a dehydrating agent, and evacuated every day for a week. At the end of this time the odor of ether had disappared. The resulting solid was a beautuful yellowish crystalline solid. The solid was kept in a vacuum dessicator to prevent it from hydrolyzing in contact with the water vapor in the air.

III. ANALYSIS OF POTASSIUM PYRROL FOR POTASSIUM.

One-half of a gram of potassium pyrrol was accurately weighed out into a 250 cc. casserole. This size casserole is necessary in order to prevent loss of the solid by "spattering". Ten cubic centimeters of concentrated sulfuric acid (C.P.) was added to the solid. The resulting solution was heater over an asbestos gauze until a black tarry substance was formed. To this mass 5 cc. of concentrated nitric acid (C.P.) was added (it is necessary to cool the tarry mass before adding the nitric acid because otherwise "spattering" will occur). The solution was again heated until all of the nitric acid was driven off and fumes of SO_3 began to come off. The solution was cooled, 5 cc. more of nitric acid added, and heated as before. The above process was repeated until the solution remaining after the nitric acid was driven off was a straw color or almost clear. This treatment "chews up" the organic matter and forms potassium sulfate and potassium bisulfate from the potassium of the potassium pyrrol and sulfate from the sulfuric acid.

After the solution had become straw colored, it

was evaporated to dryness over a very small flame. The resulting solid was cooled, taken up with 3 cc. of hot water, and filtered into a weighed silica crucible. The precipitate remaining on the filter paper was washed five times with small amounts of hot water. The combined filtrate and washings were evaporated down to dryness on the steam bath. The crucible containing the white solid was placed on a ring burner, a pinch of ammonium carbonate was added to it to convert the potassium acid sulfate to potassium sulfate, and the ammonium salts driven off by heating very gradually. The temperature of the crucible was gradually raised until the crucible was a dull red color. The crucible was cooled in a dessicator and weighed as potassium sulfate. The weight of potassium was calculated from the weight of potassium sulfate, and thus the percent of potassium in the potassium pyrrol was obtained by dividing the weight of the potassium by the weight of the potassium pyrrol taken for analysis and multiplying by a hundred.

The following are results of the analysis of potassium pyrrol for potassium by the method just described:

Wt. of C_4H_4NK	Wt K_2SO_4	% K	% of theory
.2382 gm.	.1915 gm.	36.2	97.0
.2752 gm.	.2163 gm.	35.3	95.0
.2912 gm.	.2298 gm.	35.3	95.0
.3517 gm.	.2695 gm.	34.4	92.6
.2484 gm	.1797 gm.	32.6	87.8
.4324 gm.	.3341 gm.	34.6	93.2
.2580 gm.	.1999 gm.	34.6	93.2
.4206 gm.	.3245 gm.	34.64	93.2
	Average --	34.71%	93.5%

The percentage of potassium in potassium pyrrol calculated from the formula C_4H_4NK is 37.18%.

IV. ANALYSIS OF POTASSIUM PYRROL BY USE OF IODINE SOLUTION.

By the iodination of pyrrol in the presence of caustic potash tetraiodopyrrol has been obtained by Ciamician and Selber (3). The same compound is also obtained by the action of iodine in potassium pyrrol (4).

It has been found that tetraiodopyrrol is produced in quantitative yield by the action of iodine on potassium pyrrol dissolved in ammonia (5) . It has been found that the reaction could be used as a method for the volumetric estimation of potassium pyrrol. For the preparation of tetraiodopyrrol, 5 grams of potassium pyrrol is shaken up with 10 cc. of ammonia and 100 cc. of water. To this the iodine solution is gradually added, and as the addition of iodine solution is continued, a voluminous white precipitate is obtained which appears to be little dirty. When no more iodine is taken up, the precipitate is filtered, washed and crystallized from glacial acetic acid below 100 degrees centigrade. It is obtained in beautiful yellowish crystals melting with decomposition between 140 and 150 degrees centigrade.

(3). Ciamician and Selber; Ber.;18:1766 (1885).
(4). Ciamician and Denstedt; Ber.; 15:2582 (1882).
(5). Lal Datta and Prosad; J.A.C.S.; 39:451 (1917).

Albert J. Plummer used the above method in his work on pyrrol *. The reader is referred to his thesis for the details on the analysis of pyrrol by means of iodine.

For the volumetric estimation of potassium pyrrol, the following details were carried out (5): 20 cc. of concentrated ammonium hydroxide were placed in a 250 cc. volumetric flask with 50 cc. of water. A funnel was placed in the top of the flask. 0.4 gm. of potassium pyrrol was weighed out into the funnel and washed immediately into the flask with 150 cc. of water. The flask was filled to the mark and stoppered. The solution was shaken thoroughly so the solution would be of uniform concentration. 25 cc. of the solution was drawn from the flask by means of a 25 cc. pipette and placed in a 125 cc. Erlenmeyer flask. The sample was diluted with 25 cc. of water and titrated immediately with standard iodine solution (.1 N.). An outside indicator of freshly prepared starch solution was used to determine the end point.

* Plummer, Albert J. ; Thesis "Purification and Properties of Pyrrol". B.U. Library.

(5). Lal Datta and Prosad; J.A.C.S. ; 39:451 (1917).

The following equations represent the chemical action involved in the above analysis:

$$C_4H_4NK + H_2O \longrightarrow C_4H_4NH + KOH$$

$$C_4H_4NH + 4I_2 + 4NH_3 \longrightarrow C_4I_4NH + 4NH_4I$$

It is evident from the equation that the potassium pyrrol molecule is equivalent to eight atoms of iodine. The purity of the potassium pyrrol is found by determining the ratio of the number of cubic centimeters of iodine which reacts with the potassium pyrrol of given weight, to the number with which a pure sample would react.

The following are results obtained by the analysis of potassium pyrrol with a standard iodine solution; .3374 gm. of potassium pyrrol being diluted to 250 cc. :

cc. taken		cc. iodine (.1068 N.)	% C_4H_4NK
25		20.20	84.09%
25		20.15	84.07%
25		20.15	84.07%
25		20.14	84.07%
25		20.14	84.07%
25		20.14	84.07%
	Average	20.15	84.07%

As an alternative method samples of potassium pyrrol were weighed out and placed in an Erlenmeyer flask containing 15 cc. of ammonium hydroxide and 25 cc. of water. The resulting solution was then titrated with the standard iodine solution.

The following are results obtained when the above method was carried out:

Wt. of C_4H_4NK taken	cc. of Iodine (.3371 N.)	% C_4H_4NK
.4586 gm.	79.00	76.0%
.2018 gm.	35.20	76.5%
.1342 gm.	23.65	77.8%
	Average	76.76%

Because it seemed that some pyrrol might have been lost during the hydrolysis of the potassium pyrrol, a special technique was employed to prevent this. The special technique was carried out as follows: 10 cc. of concentrated ammonium hydroxide was placed in a 125 cc. Erlenmeyer flask with 20 cc. of water. A short test-tube with a large opening was suspended in the neck of the Erlenmeyer flask. The potassium pyrrol was transferred from the weighing bottle directly into the test-tube. A

paraffined stopper was inserted immediately in the flask and the ammoniacal solution shaken into the test-tube. In this way no pyrrol could escape and was therefore all absorbed. After the potassium pyrrol had been completely hydrolyzed, the solution was titrated directly as before with a standard iodine solution.

The following are the results obtained by employing the special technique just described:

Wt. of C_4H_4NK taken	cc. of iodine (.3371 N.)	% C_4H_4NK
.0280 gm.	4.90	77.23%
.0999 gm.	17.44	77.0 %
.1958 gm.	34.22	77.1 %
	Average	77.11%

V. ANALYSIS OF POTASSIUM PYRROL FOR CARBON AND HYDROGEN.

The percentage of carbon and hydrogen in potassium pyrrol was determined by combustion. The regular procedure for the combustion of an organic compound containing nitrogen was followed,(6).

The following are the results obtained for the percent carbon and hydrogen in potassium pyrrol:

	Theory	I	II	III	IV
%C	45.6	32.07	34.15	36.34	47.76
%H	3.8	3.87	4.45	4.31	5.01

	V	VI	VII	VIII	Average
%C	37.68	32.57	35.52	43.02	37.39
%H	3.57	3.55	3.42	2.65	3.85

(6) Fisher, H.L. ; "Laboratory Manual of Organic Chemistry". John Wiley and Sons. Inc. ; New York.

VI. ANALYSIS OF POTASSIUM PYRROL FOR NITROGEN.

The percentage of nitrogen in potassium pyrrol was determined by heating the compound in a combustion tube through which a current of carbon dioxide is passing and collecting the evolved nitrogen over potassium hydroxide and then measuring the volume of nitrogen over water, (7).

The following are the results obtained for the percent nitrogen in potassium pyrrol:

	Theory	I	II	III	IV	Average
%N	13.31	11.52	11.43	11.41	11.43	11.437

This corresponds to a purity of 86 percent potassium pyrrol.

(7) Gattermann; "Practical Methods of Organic Chemistry" Translated by Schober and Babasinian. Third American from eleventh German Edition. The MacMillian Co. New York, 1914.

VII. SOLUBILITY OF POTASSIUM PYRROL.

An attempt was made to find a solvent for potassium pyrrol so that it might be recrystallized and pure crystals obtained but unfortunately a solvent was not found amoung the organic solvents tried.

Potassium pyrrol was found to be insoluble in both cold and hot solutions of the following compounds:

Acetone
Aniline
Benzene
Carbon disulfide
Carbon tetrachloride
Choloroform
di-N-Butyl-aniline
Ether
Ethyl alcohol
Furfurgl alcohol
Furfural
Gasoline
Kerosene
Ligroin
Methyl Salicylate
Nitro-benzene
Pinene
Pyridine
Pyrrol
Triamylamine
Toluene
m-Toluidine
Turpentine
Xylene.

VIII. DISCUSSION.

Dr. Mason suggested that a mechanical stirrer be used when the potassium pyrrol was washed with ether in order to make the washings more effective. However, after careful consideration, it was decided that this process would not increase the percent purity of the potassium pyrrol more than one-half percent as it was ground finely with a blunt stirring rod during each ether washing. Increasing the purity one-half percent would not be sufficient to produce a pure compound as the results show that the potassium pyrrol is about 90 percent pure. Also lack of material and time prevented the suggestion from being carried out.

IX. SUMMARY.

Potassium pyrrol was prepared by the method described.

The following are the results obtained for the percent purity of the potassium pyrrol when it was analized for the different elements of which it is composed:

Element	Calculated	Observed	% Potassium pyrrol
K	37.18	34.71	93.5
N	13.31	11.437	86.
C	45.6	37.39	82.

Analysis with iodine solution of potassium pyrrol which was diluted to 500 cc. and a portion titrated gave a purity of 84.07 percent, while analysis of a definite weight of potassium pyrrol without diluting gave a purity of 76.76 percent and 77.11 percent.

X. CONCLUSION.

The attempts to prepare pure pyrrol have been continued and extended. The analysis show that the potassium pyrrol from which it was hoped to obtain pure pyrrol, is not itself pure. It is impossible at this point to predict the nature of the impurity, but it is obviously a compound closely related to pyrrol which reacts with potassium thus forming a compound with practically the same ratio of potassium to nitrogen as in potassium pyrrol but does not react with iodine. If this is the case the results can be explained.

It has also been concluded that this method of preparation of potassium pyrrol is not a good one.

BIBLIOGRAPHY

(1) Anderson; Annalen der Pharmacie; 105:354(1858)

(2) Ciamician and Dennstedt; Ber., 19:173(1880)

(3) Ciamician and Silber; Ber., 18:1766(1885)

(4) Ciamician and Dennstedt; Ber., 15:2582(1882)

(5) Lal Datta and Prosad; J.A.C.S., 39:451(1917)

(6) Fisher, H.L.; "Laboratory Manual of Organic Chemistry". John Wiley and Sons,Inc; New York.

(7) Gatterman; "Practical Methods of Organic Chemistry". The MacMillan Company, New York; 1914

* Plummer, Albert J.; Thesis:"Purification and properties of pyrrol", B.U.Library.

** Meyer and Jacobson; "Lehrbuch der Organischen Chemie". Walter De Gruyter & Co. Berlin and Leipzig, 1923.

The above abbreviations are standard and are authorized by the American Chemical Society.